Vibrational effect on the fragmentation dynamics of the C K-shell excited CF_2CH_2

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Abstract
Photoabsorption cross-sections of CF_2CH_2 were measured in the carbon K-edge region and linear time-of-flight mass spectra were acquired at some photon energies across the two π* peaks. The kinetic energy distributions of CH_2^+ and CF_2^+ with two components were deduced from the analysis of the mass spectra. The CH_2^+ ion with high kinetic energies increases with the extent of vibrational excitation of the C_F $1s^{-1}\pi^*$ state, indicating that molecular vibrations play an important role in the photofragmentation of the inner-shell excited molecule.

Key words: inner-shell excitation, fragmentation, vibrational effect

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1. Introduction

Studies on the photochemical dynamics of inner-shell excited molecules have been stimulated by the recent advancement of synchrotron radiation technology. Inner-shell excited molecules in a specific vibrational level can now be produced by means of synchrotron radiation. It is particularly interesting to investigate the influence of the vibronic quantum states onto the dissociation process, because a specific dissociation channel induced by the nuclear motion may be opened. Recent studies on the fragmentation of the O $1s^{-1}2b_2$-excited water molecule [1,2] demonstrate that the yield of the H_2^+ fragment ion depends on the vibrational level of the excited molecule.

Localized nature of inner-shell electrons of a molecule enables us to pump energy into a specific atomic site. On the energetics viewpoint, it is of great interest to determine whether the initial memory of inner-shell excitation preserves to result in site-selective fragmentation against the energy flow over the entire molecule. In our recent studies on the fragmentation of the inner-shell excited CF_3CN [3,4], we found dependence of the kinetic energy distribution (KED) of the fragment ions on the site of excitation. That is, the KED of the CF_3^+ ion gives only one peak when exciting a C_F 1s electron where C_F means the carbon of the CF_3 group, while it consists of at least two peaks in the excitation of the N 1s and C_N 1s electrons. We claimed that the less energetic component in the latter cases is produced after energy redistribution through the C–C≡N skeleton into the vibrational modes of the CF_3 group. The interpretation was supported by the later work with the CF_3CCH molecule [5].

In the present work we studied the KEDs of the CF_2^+ and CH_2^+ fragment ions produced by the dissociation of the C K-shell excited CF_2CH_2 molecule by means of a fitting procedure developed by Saito and Suzuki [6]. We focus here on the dependence of the KEDs on the excited vibrational energy.

2. Experimental

The experiments were performed on the soft X-ray photochemistry beamline BL27SU [7,8] at the SPring-8 facility in Japan. Photoabsorption cross-sections were measured in the range of 283–310 eV with a resolving power of ≈ 9500. A Samson-type ion chamber with 10-cm long electrodes was mounted on the main chamber. Photoion currents from the two cathode plates were fed to a pair of picoammeters and stored in a personal computer, together with the sample pressure. Time-of-flight (TOF) mass spectra of the fragment ions were acquired with the photon bandpass $\Delta E \approx 45$ meV. In the present study we measured linear-TOF mass spectra at photon energies of 285.4, 285.8 and 286.5 eV to across the peak of the C_H 1s $\rightarrow \pi^*$ transition, and of 289.6, 290.0 and 290.3 eV to across that of C_F 1s $\rightarrow \pi^*$. The method was based on a total photoelectron–photoion coincidence technique. An effusive flow of sample gas was introduced into the main chamber through a gas nozzle orthogonal to both the photon beam axis and the TOF tube. The pressure in the chamber during the measurements was kept 4×10^{-4} Pa.

3. Results and discussion

The total photoabsorption cross-section of CF_2CH_2 in the C K-edge is shown in Fig. 1. Distinct peaks observed in 285–286 and 289–290 eV have been assigned to the promotion to the π^* orbital from the C_H 1s and C_F 1s electrons, respectively [9]. The peaks have asymmetric shapes and thus we can see that the transitions are accompanied by the vibrational progressions. The vibrational spacing of 370 meV is embedded in the peaks when we analyse the spectrum by use of the least-squares curve fitting with Voigt functions. The vibrational mode is probably the C–H stretching or overtone of the C–C–H bending. Also, Rydberg transitions are reasonably assigned in this work. Detailed discussion on the peak assignment will be given elsewhere.

Linear-TOF mass spectra were measured to deduce kinetic energies of the CH_2^+ and CF_2^+ fragment ions. A typical spectrum obtained at 289.6 eV is shown in Fig. 2. The spectrum is somewhat different from that reported by Habenicht et al. [10] because of the different experimental technique employed. Some peaks are sharp and others are broad. Kinetic energy of each fragment ion is reflected in the peak width. Thus, the KED has been obtained through a fitting calculation of time-of-flight spectra of these ions, in which angular distributions and kinetic energies of the ions were considered [3-6].

Figure 3 shows the KEDs for the CH_2^+ and CF_2^+ fragment ions superimposed for measured different photon energies. The upper panels are for the C_F 1s → π* transition and the lower ones are for the C_H 1s → π*. Each KED is normalized with respect to its area. The KED consists of at least two components fitted by the Gaussian functions. The maxima of the main peaks for the CH_2^+ and CF_2^+ ions are found to be 3.9 and 1.4 eV, respectively. The CH_2^+ ion with low kinetic energy has a higher yield at the upper panel (C_F 1s excitation) than that at the lower (C_H 1s excitation). As shown at the upper, this CH_2^+ ion at C_F 1s may originate in intramolecular energy relaxation from the initially excited C_F 1s into vibrational modes of CH_2, as discussed in our previous studies [3-5]. The vibrational excitation probably results in little change in the low kinetic energy component of CH_2^+. The high kinetic energy component, however, gets larger in the KED of CH_2^+ as shown in the upper panel of Fig. 3. This finding means that the vibrational excitation decreases action of the CH_2 group as an intramolecular energy reservoir and results in the promotion of the direct dissociation to form the energetic CH_2^+ ion. Thus, the yield of the CH_2^+ ion with kinetic energy centred at 3.9 eV increases with the extent of vibrational excitation in the case of the C_F 1s excitation.

For the C_H 1s → π* transition, on the contrary, the KEDs of CH_2^+ and CF_2^+ do not change irrespective of the extent of vibrational excitation as shown in the lower panels of Fig. 3. In this case, vibrational excitation of the C–H and C–C–H modes does not affect a dissociation process probably because of small quantity of energy compared to the energy of a molecular ion with repulsive potential surfaces imparted through the C_H 1s excitation.

From the present findings it is clear that molecular vibrations play an important role in the photofragmentation of the inner-shell excited molecule of CF_2CH_2. The vibrational excitation induces the direct dissociation process in the case of the C_F 1s excitation. Further experimental evidence is necessary for complete understanding of the effect of molecular vibration on the dissociation process.

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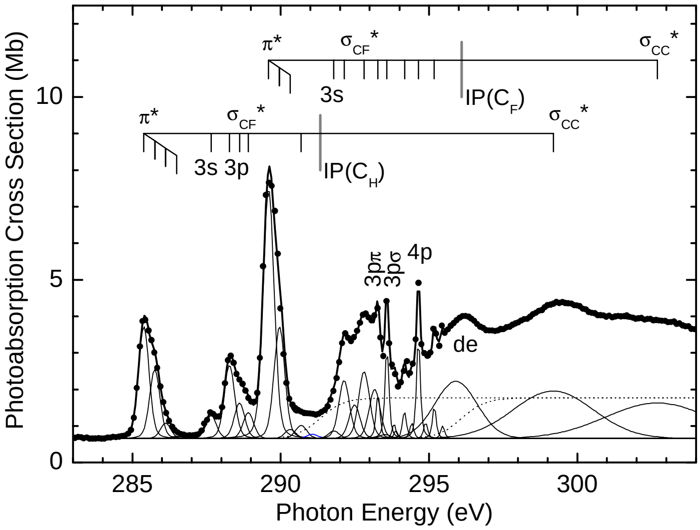

Fig. 1. Total photoabsorption cross-sections of CF_2CH_2 in the C K-shell excitation region. Circles are the experimental data and solid curves are obtained by the least-squares curve fitting. Peak assignments are also given in the figure. The "de" means double excitation.

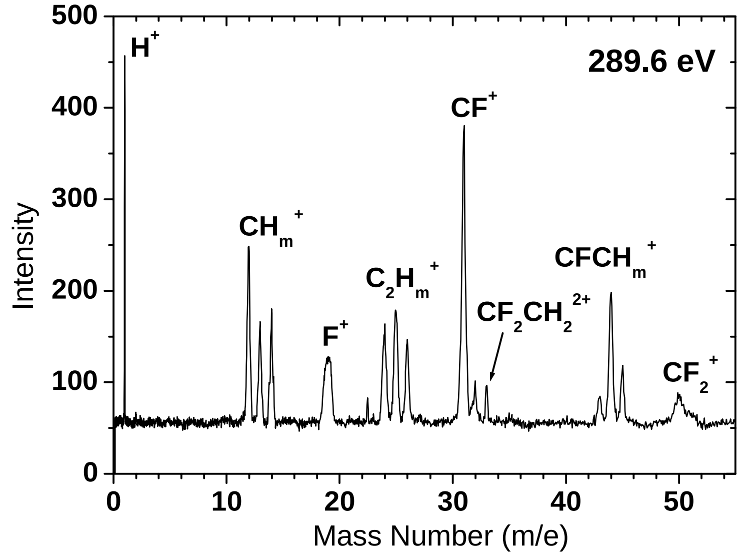

Fig. 2. Linear-TOF mass spectrum observed in the C_F 1s → π* transition of CF_2CH_2 at 289.6 eV.

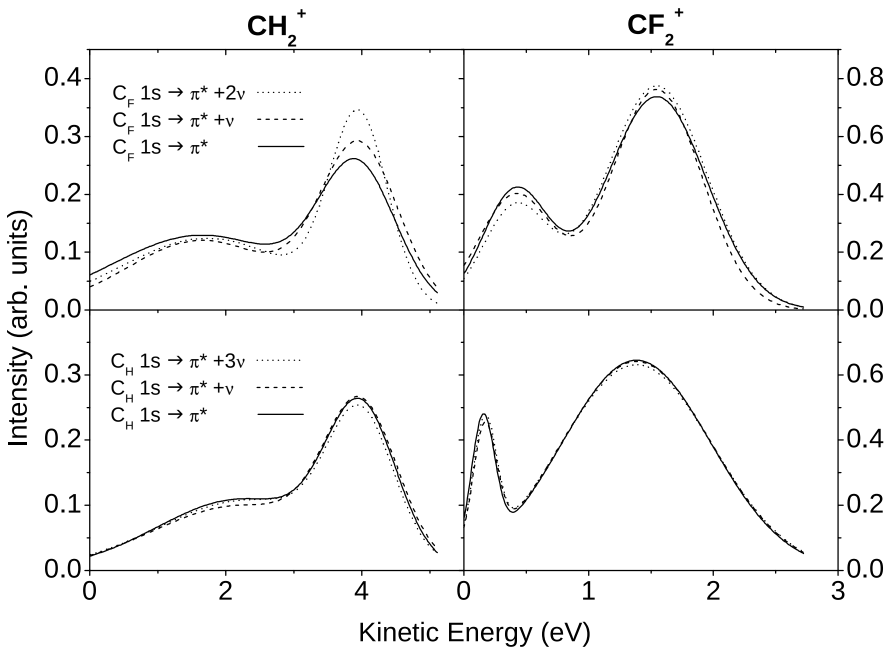

Fig. 3. Kinetic energy distributions of the CH_2^+ and CF_2^+ fragment ions observed by exciting the C_F 1s electron (upper panels) and the C_H 1s electron (lower panels) of CF_2CH_2.

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